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A new method of evaluating anharmonicity constants of polyatomic molecules

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A new method of evaluating anharmonicity constants utilising the technique of parametric representation by Jordanov and Nikolova has been developed. This method has been verified in some simple molecules.

1. INTRODUCTION

One of the important aspects in molecular vibrational problems is the determination of anharmonicity effect upon vibrational frequencies. Pioneer work on the determination of anharmonicity constant was carried out by Dennison (1940) where observed isotopic frequencies and Coriolis zeta constants were made use of. Curtis (1964) developed a new procedure for the calculation of anharmonicity factor using mean amplitudes of vibration and the best fit force field. In the present paper an attempt has been made to calculate the anharmonicity constants and hence harmonic wavenumbers by parametric representation method.

2. THEORETICAL CONSIDERATION

The well known secular equation for molecular vibration is (Wilson Jr. *et al* 1955)

$$GFL = L\Lambda \qquad \ldots (1)$$

where G is the inverse kinetic energy matrix, F is the potential energy matrix, Λ is the diagonal matrix of vibrational eigen values with elements $\Lambda_k = 4\pi^2c^2\nu_k^2$ [c is the velocity of light in vacuum and ν_k is the vibrational wave number of the k-th mode] and L is the eigen vector matrix obeying the normalising condition

$$L\tilde{L} = G. \qquad \ldots (2)$$

In the parametric representation method of Torok & Pulay (1965, 1966) L matrix is written as

$$L = L_0A \qquad \ldots (3)$$

where L_0 is known as the initial matrix (Jordanov & Nikolova 1972, 1973a, 1973b) defined as (Billes 1966)

$$L_0 = V\tau^{\frac{1}{2}}$$

where V is the eigen vector of G and $\tau^{\frac{1}{2}}$ is the diagonal matrix of positive square roots of eigen values of G and A is a proper orthogonal parameter matrix. For 2×2 case A is chosen to be

$$A = \begin{vmatrix} \cos\phi & \sin\phi \\ \sin\phi & \cos\phi \end{vmatrix} \tag{4}$$

Differential form of eq. (1) as given by Jordanov & Nikolova (1972) is

$$\Delta\Lambda = [L^{-1}\Delta G\,\tilde{L}^{-1}\Lambda]+[\tilde{L}\Delta F L]+[\Lambda(L^{-1}\Delta L)-(L^{-1}\Delta L)\Lambda] \quad \ldots (5)$$

or

$$\Delta\Lambda = K+D+M \quad \ldots (6)$$

where

$$K = L^{-1}\Delta G\,\tilde{L}^{-1}\Lambda$$

$$D = \tilde{L}\Delta F L$$

and

$$M = \Lambda(L^{-1}\Delta L)-(L^{-1}\Delta L)\Lambda.$$

It is evident from eq. (6) that a small change in the eigen value matrix $\Delta\Lambda$, is distributed among three terms : kinetic K, dynamic D and mixing M.

M is a matrix with zero diagonal elements, does not contribute to $\Delta\Lambda$. Hence the sum of off-diagonal elements of K, D and M is zero.

For isotopic substitution

$$F = 0 \quad \text{or} \quad D = 0.$$

Hence

$$\Delta\Lambda = K+M. \quad \ldots (7)$$

The calculated frequency shifts are evaluated from the diagonal elements of K

$$\Delta\Lambda_i = K_{ii}. \quad \ldots (8)$$

The off-diagonal elements of K and M are linked by the relationship

$$K_{ij} = -M_{ij}. \quad \ldots (9)$$

The elements of K and M are connected to L through A and it is possible to choose A by the use of experimental isotopic shifts.

Putting $B = L_0^{-1}\Delta G\tilde{L}_0^{-1}$, the equation $K = L^{-1}\Delta G\tilde{L}^{-1}\Lambda$ can be written as

$$\frac{K}{\Lambda} = \tilde{A}BA \tag{10}$$

after a simple mathematical manipulation. This equation gives the parametrised form of isotopic frequencies expressed through the geometry of the molecule.

For second order problems expansion of eq. (10) leads to

$$\frac{K_{11}}{\Lambda_1} = B_{11}C_\phi^2+B_{22}S_\phi^2-2B_{12}S_\phi C_\phi \tag{11}$$

$$\frac{K_{22}}{\Lambda_2} = B_{11}S_\phi{}^2+B_{22}C_\phi{}^2+2B_{12}S_\phi C_\phi \quad \ldots (12)$$

and

$$\tan\phi_1 = \frac{B_{12}\pm\sqrt{B_{12}{}^2-\left(B_{11}-\frac{K_{11}}{\Lambda_1}\right)\left(B_{22}-\frac{K_{11}}{\Lambda_1}\right)}}{B_{22}-\frac{K_{11}}{\Lambda_1}} \quad \ldots (13)$$

$$\tan\phi_2 = \frac{-B_{12}\pm\sqrt{B_{12}{}^2-\left(B_{11}-\frac{K_{11}}{\Lambda_1}\right)\left(B_{22}-\frac{K_{22}}{\Lambda_2}\right)}}{B_{11}-\frac{K_{22}}{\Lambda_2}} \quad \ldots (14)$$

where C_ϕ and S_ϕ denote the cosine and sine of the angle ϕ.

From eqs. (11) and (12) it is clear that

$$\frac{K_{11}}{\Lambda_1}+\frac{K_{22}}{\Lambda_2} = B_{11}+B_{22}. \quad (15)$$

This equation establishes the equality between the theoretically predicted sum and experimentally observed sum of isotopic frequencies. Any discrepancy in these two sums result in two distinct solutions for ϕ i.e., $\phi_1 \neq \phi_2$. This discrepancy may be attributed to the anharmonicity of vibrations. From Table 1 it is evident that the difference between the two sums, say Δ, it small in the case of molecules where the product rule is obeyed and large in the case of molecules where the product rule is not obeyed. Hence the difference between the two sums may be legitimately be assumed as due to anharmonicity of vibrations.

This Δ gives the total anharmonicity effect for the system under consideration. Exact knowledge about the distribution of this total effect Δ among the two K/Λ's yields the correct value for the anharmonicity correction for both the individual frequencies. Assuming x per cent of Δ is contributed to K_{11}/Λ_1 and remaining to K_{22}/Λ_2, the distribution of Δ can be studied graphically. Consequently eqs. (13) and (14) can be rewritten in terms of x as

$$\tan\phi_1 = \frac{B_{12}\pm\sqrt{B_{12}{}^2-\left[B_{11}-\left(\frac{K_{11}}{\Lambda_1}+\frac{\Delta x}{100}\right)\right]\left[B_{22}-\left(\frac{K_{11}}{\Lambda_1}+\frac{\Delta x}{100}\right)\right]}}{B_{22}-\left(\frac{K_{11}}{\Lambda_1}+\frac{\Delta x}{100}\right)} \quad \ldots (16)$$

and

$$\tan\phi_2 = \frac{-B_{12}\pm\sqrt{B_{12}{}^2-\left[B_{11}-\left(\frac{K_{22}}{\Lambda_2}+\frac{100-x}{100}\Delta\right)\right]\left[B_{22}-\left(\frac{K_{22}}{\Lambda_2}+\frac{100-x}{100}\Delta\right)\right]}}{B_{11}-\left(\frac{K_{22}}{\Lambda_2}+\frac{100-x}{100}\Delta\right)}$$

$$\ldots (17)$$

The physical significance of these two equations is that they establish the equality between ϕ_1 and ϕ_2 and hence any one of these two equations can be used. Further graphical representation of force constants with x, the percentage of correction, is rendered feasible by varying x from 0 to 100. The maxima of the curve is taken to be the proper correction for the system under consideration.

Table 1. The difference Δ between the theoretically predicted sum and experimentally observed sum of isotopic frequencies for various molecules.

Molecule	$\frac{\lvert G\rvert}{\lvert G^*\rvert}$	$\frac{\nu_i\nu_j}{\nu_i^{*2}\nu_j^{*2}}$	Δ
$^{116}SnCl_4$—$^{124}SnCl_4$	1·036603	1·036039	0·00005
$^{28}SiF_4$—$^{29}SiF_4$	1·025871	1·025883	0·00010
$^{12}CH_4$—$^{13}CH_4$	1·02310	1·01856	0·00090
NH_3—ND_3			
a species	3·393850	3·058900	0·056819
e species	3·510198	3·392260	0·016131
H_2O—D_2O	3·59244	3·43110	0·023117
CH_4—CD_4	3·192768	3·070870	0·015186
SiH_4—SiD_4	3·547749	3·390573	0·022712
GeH_4—GeD_4	3·79448	3·642973	0·020856
AsH_3—AsD_3			
a species	3·850601	3·637471	0·029336
e species	3·919305	3·804437	0·015155
PH_3—PD_3			
a species	3·673271	3·472555	0·028842
e species	3·805432	3·690212	0·015607

With the help of the proper percentage of correction K/Λ is corrected. Following relations given by Dennison (1940) are used for the calculation of anharmonicity constant

$$\nu_i = \omega_i(1-\alpha_i) \qquad \ldots (18)$$

$$\nu_i^* = \omega_i^* \left(1-\frac{\omega_i^*}{\omega_i}\alpha_i\right) \qquad \ldots (19)$$

where α_i is the anharmonicity constant, ν and ν_i^* are anharmonic frequencies of parent and isotopic molecule and ω_i and ω_i^* are harmonic frequencies of parent and isotopic molecule.

Incorporating eqs. (18) and (19) in the relation

$$\frac{K}{\Lambda} \quad \frac{\omega^{*}-\omega^{*2}}{\omega^{2}} \tag{20}$$

an expression for α is derived as

$$\alpha_1 = \frac{1-c_1 \frac{\nu_1}{\nu^*}}{1-c_1} \tag{21}$$

and

$$\alpha_2 = \frac{1-c_2}{1-c_2} \tag{22}$$

where

$$c_1 = \sqrt{1-\left(\frac{K_{11}}{\Lambda_1}\right)_{\omega\nu}} \text{ and } \quad c_2 = \sqrt{1-\left(\frac{K_{22}}{\Lambda_2}\right)_{\omega\nu}}$$

Using this anharmonicity constant, the observed frequencies were corrected for anharmonicity effect.

3. Results and Discussion

Procedure given above has been applied to determine the anharmonicity constants for some simple isotopic pairs such as H_2O-D_2O, CH_4-CD_4, GeH_4-GeD_4,

Table 2. Calculated harmonic wavenumbers (cm^{-1}) for various molecules.

	GeH_4–GeD_4		SiH_4–SiD_4		NH_3–ND_3		AsH_3–AsD_3		PH_3–PD_4		H_2O–D_2O	
	P.S.	Ref. (*)	P.S.	Ref. (*)	P.S.	Ref. (**)	P.S.	Ref. (**)	P.S.	Ref. (**)	P.S.	Ref. (***)
ω_1	—	—	—	—	3510	3540	2203	2209	2490	2448	3836	3832
ω_1^*	—	—	—	—	2510	2527	1568	1571	1781	1760	2766	2783
ω_2	—	—	—	—	1118	1055	963	972	1020	1045	1646	1648
ω_2^*	—	—	—	—	948	812	690	695	746	759	1206	1206
ω_3	2183	2195	2278	2312	3624	3547	2213	2225	2404	2390	—	—
ω_3^*	1558	1584	1643	1673	2654	2612	1575	1580	1727	1720	—	—
ω_4	852	846	951	940	1637	1676	1013	1012	1146	1153	—	—
ω_4^*	613	610	701	690	1196	1217	719	718	818	822	—	—

P.S.—Present Study
Ref.(*) —Duncan J. L. and Mills I. M. (1964)
Ref.(**) —DeAlti *et al* (1964)
Ref.(***)—Benedict *et al* (1956).

SiH_4-SiD_4, NH_3-ND_3, PH_3-PD_3 and AsH_3-$As.D_3$. In all these cases graphs were drawn between force constants and percentage of correction x. A typical curve is shown in figure 1. It is easily seen that variation of force constant

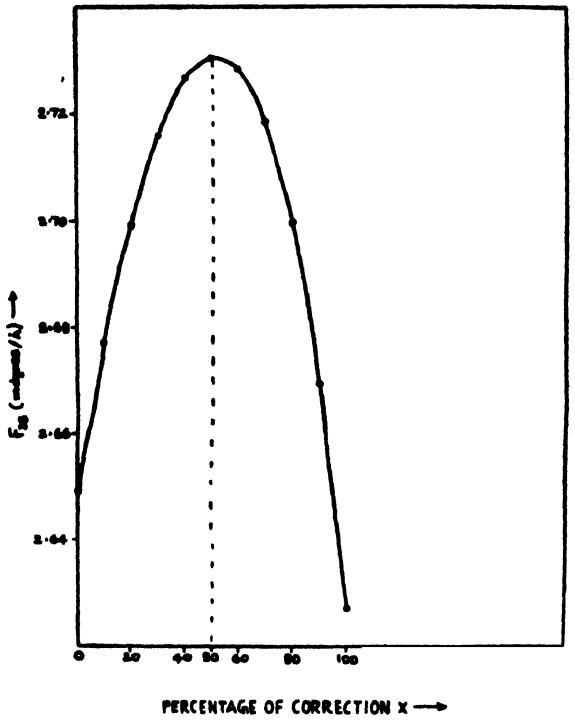

Fig. 1. Variation of stretching force constant F_{33} with percentage of correction x for SiH_4–SiD_4 isotopic pair.

with percentage of correction is considerably large in all the isotopic pairs except CH_4–CD_4 pair. In the latter case, the graph does not give rise to a maxima as in the other isotopic pairs, thereby rendering it impossible to calculate the anharmonicity constant for CH_4–CD_4 pair utilising this method. Using the eqs. (21) and (22), the anharmonicity constants were determined, with the help of which harmonic frequencies were computed. The results are in very good agreement with previous literature values and are presented in Table 2.

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